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SHORT COMMUNICATIONS

Electron Heat Capacity and Lattice Properties of Americium

A. A. Povzner*, A. N. Filanovich, V. A. Os'kina, and A. G. Volkov

El'tsyn Ural Federal University, ul. Mira 19, Yekaterinburg, 620002 Russia
**e-mail: a.a.povzner@ustu.ru*

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Abstract—The temperature dependence of the electron heat capacity of americium is calculated using the concepts on the electronic structure and magnetic properties of this element. The Debye temperature, the thermal expansion coefficient, and the bulk modulus of americium are determined on the basis of the results of calculations and experimental data on heat capacity.

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The study of the origin of anomalous thermal and physical properties of americium is of great theoretical and practical importance. On the one hand, such knowledge is essential for determining the concentration and type of defects appearing as a result of radioactive decay [1]. On the other hand, concentration- and temperature instabilities to superconductivity and magnetic ordering appear in the strongly correlated electronic subsystem of americium [2], and the parameters of interaction of collectivized electrons are close to the values for which the metal–insulator transition takes place [2].

Information on the lattice properties of americium is scarce and contradictory [3–7]. Experimental data on the thermal expansion coefficient and the bulk modulus are limited in temperature and are available only for the ^{243}Am. The phonon spectrum has been calculated only for the fcc phase of AmII [8], which is observed only under a high external pressure [2], while the AmI crystal structure is formed under standard conditions. Semi-empirical simulation of the specific heat of americium was carried out in [9]; however, analysis was carried out only for high temperatures under the assumption that the lattice heat capacity at constant volume is described by the Dulong–Petit law. In addition, analysis performed in [9] is limited to the heat capacity, while a more detailed treatment requires the calculation of a complex of properties based on a unified model.

In this communication, we present self-consistent analysis of thermodynamic properties of americium taking into account not only lattice anharmonism, but also the features of its strongly correlated electronic subsystem. It was shown earlier that noticeable spin-fluctuation effects appear in calculations of the electronic structure and the spin magnetic susceptibility in the strongly correlated subsystem of d, f-electrons in americium [10], which must make a significant contribution to the formation of its electron heat capacity.

The molar Gibbs thermodynamic potential (TDP) in the model considered here can be represented by the sum $\Phi = \Phi_0 + \Phi_{ph} + \Phi_{el}$, where $\Phi_0 = \Phi_0(P)$ is the temperature-independent part of the thermodynamic potential (which, however, depends on pressure); the phonon part of the potential is described by the expression

$$\Phi_{ph} = 3R(3/8\theta + T\phi(z)), \quad (1)$$

where T is the temperature, θ is the Debye temperature, $z = \theta/T$, $\phi(z) = \ln(1 - e^{-z}) - D(z)/3$, $D(z)$ being the standard Debye function. The electron part of the thermodynamic potential [11] can be written in the form

$$\Phi_{el} = T\sum_{l=f,d}\ln\int_{-\infty}^{\infty}\sum_{a=\pm1} g_0^{(l)}(\varepsilon + U^{(l)}n_l + \alpha\xi) \times \ln\left(1 - \exp\left(\frac{\varepsilon - \mu}{T}\right)\right)d\varepsilon + \Phi_m, \quad (2)$$

where $l = f, d$ is the band index; $U^{(l)}$ is the parameter of the Hubbard repulsion of electrons of the l band; $g_0^{(l)}(\varepsilon)$ is the density of states of the l band, calculated in accordance with the LDA + U + SO scheme (in the full-potential linearized augmented plane wave (FP-LAPW) method); μ is the chemical potential of electrons determined from the electroneutrality condition $2\sum_l n_l = \sum_l\sum_{\alpha=\pm1}\int g_0^{(l)}(\varepsilon + U^l n_l + \alpha\xi_l) f_{FD}(\varepsilon - \mu/T)d\varepsilon$; f_{FD} is the Fermi–Dirac function; $\alpha = \pm1$; T is the temperature, which is expressed here and in Eq. (3) in the energy units (i.e., is multiplied by the Boltzmann constant in electronvolts, which is equal to 0.8625×10^{-4} eV/K); $2n_l$ is the filling factor of the l band; and

$\xi_l^2 = \sum_{\gamma = \pm z} \xi_{l,\gamma}^2$ is the mean square of the modulus of the random onsite exchange field (see [10, 11]).

The contribution to the TDP associated with paramagnons and their interaction has the form

$$\Phi_m = \sum_l \chi_\parallel^{(l)} \xi_l^2 + \sum_l k_l \xi_l^4 / U^{(l)} + \sum_{\mathbf{q}, l, \gamma} \oint d\omega \tanh(\omega/2T) \ln(D^{(l)^{-1}} + X(\mathbf{q}, \omega)), \quad (3)$$

where $k^{(l)} = \partial^2 \Phi_{el}/\partial \xi^2 = U^{(l)}(\chi_\perp^{(l)} - \chi_\parallel^{(l)})/\xi_l^2$ is the spin stiffness that characterizes the extent of manifestation of magnetic anharmonism, and $X(\mathbf{q}, \omega)$ is the Lindhard function.

Electron heat capacity $C_{el}(T)$ is determined in terms of the second derivative of electron free energy (2) with respect to temperature and has the form

$$C_{el}(T) = R\left(C_{elo} + \sum_{l=2,3} C_f^{(l)} + \sum_{l=2,3} C_{eff}^{(l)}\right), \quad (4)$$

where $C_{elo} = \frac{\pi^2}{3} \sum_{l=0}^{3} \sum_{\alpha = \pm 1} g_\alpha^{(l)} T$ is the "one-electron" contribution taking into account magnetic anharmonism leading to splitting of electron energies in fluctuating exchange fields, and the "fluctuation" and the "electron–fluctuation" contributions are $C_f^{(l)} \sim U^{(k)} m^{(l)} \frac{dm^{(l)}}{dT}$ and $C_{eff}^{(l)} \sim U^{(l)} \frac{dm^{(l)}}{dT}\left(T \sum_\alpha g_\alpha^{(l)}\right)$ with $l \neq l'$, respectively; $g_\alpha^{(l)} = g_0^{(l)}\left(\mu + \frac{1}{2} U^{(l)} n_l + \alpha U^{(l)} m^{(l)}\right)$, $g_\alpha^{(l')} = g_0^{(l')}(\mu + \alpha I m^{(l')})$; and $m^{(l')}$ is the squared amplitude of spin fluctuations, which is calculated using the fluctuation–dissipation theorem [10, 11].

In accordance with earlier calculations of the magnetic susceptibility of americium [10], the correlation radius $R_C^{(l')} = (a^{(l)} D^{(l)})^{1/2}$ of spin density of f and d electrons (where $a_l (\sim 0.1)$ is the spatial inhomogeneity parameter of the Lindhard function) above $T_{fl}^{(f)} = 75$ K and $T_{fl}^{(d)} = 45$ K, respectively, turns out to be not larger than the interatomic spacing. As a result, we can disregard interstitial spin density correlations in the system of f and then d electrons at $T > T_{fl}^{(f)}$ and then at $T > T_{fl}^{(d)}$, and term $C_f^{(l)}$ in Eq. (4), which is associated with paramagnon excitations, vanishes in proportion to $1/T$.

In addition, in accordance with relation (1), we can write the following expression for the lattice component of heat capacity:

$$C(T) = -T\frac{\partial^2 \Phi}{\partial T^2} = 3R\left\{C_{VR}(z)\left[1 - \frac{1}{z}\left(\frac{\partial \theta}{\partial \theta}\right)_P\right]^2 - T\left[\frac{3}{8} + \frac{D(z)}{z}\right]\left(\frac{\partial^2 \theta}{\partial T^2}\right)_P\right\}, \quad (5)$$

where $C_{VR}(z)$ is the standard Debye heat capacity normalized to $3R$, $D(z)$ is the Debye function, and the Debye temperature generally depends on the temperature of the ambient.

The expression for volume thermal expansion coefficient O and bulk modulus K obtained in such an approach on the basis of the phonon contribution to TDP (1) have the form

$$O = -\frac{3R\theta\gamma_\theta}{VK}\left\{C_{VR}(z)\left[1 - \frac{T}{\theta}\left(\frac{\partial \theta}{\partial T}\right)_P\right]\frac{1}{\theta} + \left[\frac{3}{8} + \frac{D(z)}{z}\right]\left[\frac{1}{\theta}\left(\frac{\partial \theta}{\partial T}\right) + \frac{1}{\gamma_\theta}\left(\frac{\partial \gamma_\theta}{\partial T}\right)_P - \frac{1}{B}\left(\frac{\partial K}{\partial T}\right)_P\right]\right\}, \quad (6)$$

$$K = K_0 + K_P = K_0 + \frac{3R}{V}\left\{\frac{3}{8}\gamma_\theta^* \theta - T[\gamma_\theta^2 C_{VR}(\theta/T) - \gamma_\theta^* D(\theta/T)]\right\}. \quad (7)$$

Parameters γ_θ and γ_θ^* appearing in these relations are the generalized Grüneisen parameters [12], and the Debye temperature is calculated by the formula

$$\theta = \frac{\hbar}{k_B}(6\pi^2 N_A^2)^{1/3} \sqrt{\frac{3}{\mu}} \Theta^{1/2} K^{1/2} V^{1/6}, \quad (8)$$

where μ is the molar mass; K is the bulk modulus; V is the molar volume; $\hbar$, k_B, and N_A are the Planck and Boltzmann constants and the Avogadro number; and Θ is an auxiliary function depending on Poisson ratio σ characterizing the ratio of shear modulus G to bulk compression modulus K.

Figure 1 shows the electron heat capacity obtained from self-consistent calculation of the density of electron states and spin magnetic susceptibility [10]. It can be seen that the paramagnetic contribution increasing in the spin-fluctuation temperature interval, which is responsible for the peak in the electron heat capacity, is significant in the low-temperature range. After the attainment of temperatures $T_{fl}^{(d)}$ and $T_{fl}^{(f)}$, the specific heat of americium is mainly determined by the one-electron contribution, which is calculated taking into account the renormalization of the density of states by spin fluctuations ($\gamma = 4$ mJ/(mol K)) and which is shown by the dashed line in Fig. 1.

Using the resultant temperature dependence of the electron heat capacity, the temperature dependence of the lattice heat capacity (squares in Fig. 2) was determined from the condition of the best agreement

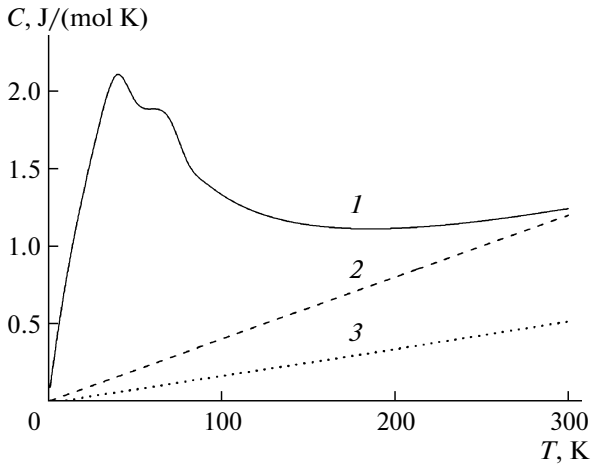

Fig. 1. Temperature dependence of various contributions to the specific heat capacity of americium (results of our calculations): electron contribution (*1*); one-electron contribution renormalized by spin fluctuations (*2*); and contribution of phonon anharmonism (*3*).

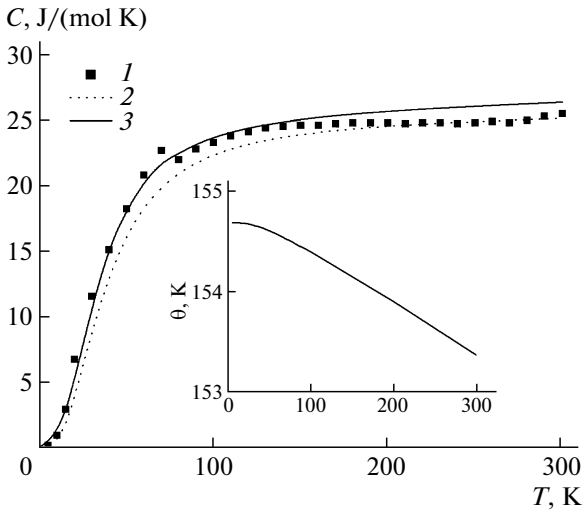

Fig. 2. Temperature dependence of the specific heat capacity of americium: experimental data [3] (*1*), lattice component (our calculations) (*2*), and total heat capacity (our calculations) (*3*); the inset shows the Debye temperature of americium (our calculations).

between the experimental data and the results of calculations. This, in turn, has made it possible to determine the parameters characterizing the phonon anharmonism of americium and its Debye temperature. The contribution of the phonon anharmonism to the specific heat of americium is also shown in Fig. 1, which means that the electronic subsystem affects the specific heat of americium more strongly than the phonon anharmonism in the entire temperature interval under investigation. In Fig. 2, the results of calculation of the total specific heat capacity of americium are compared with the available experimental data [3]; it can be seen that the experimental data can be described quite exactly using the model under investigation. It is important to note that the values obtained for the Debye temperature (see the inset to Fig. 2) are higher than the values obtained in [3], which vary from 100 to 130 K. This is due to the fact that the low-temperature electron heat capacity was not taken into account correctly in [3], which resulted in exaggerated values of the lattice contribution and, hence, of the Debye temperature.

The values obtained for the lattice parameters of americium formed the basis for calculating the temperature dependences of the lattice components of its linear thermal expansion coefficient (LTEC) α and bulk modulus shown in Fig. 3.

In accordance with our estimates of the temperature dependence of the LTEC and bulk modulus, americium exhibits a relatively weak (as compared to neptunium and plutonium [13]) lattice anharmonism, which is in conformity with the observed contribution of the phonon anharmonism to the heat capacity and is confirmed by the low value of lattice Grüneisen parameter $\Gamma = -\dfrac{\partial \ln \theta}{\partial \ln V}$ for americium, which does not exceed 0.54 in the temperature interval up to 400 K in accordance with our calculations.

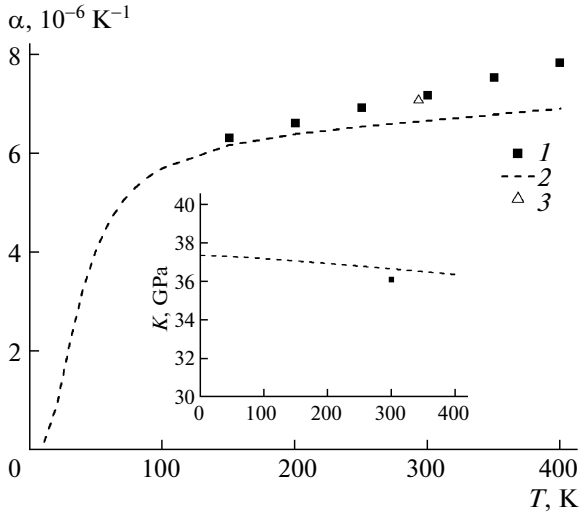

Fig. 3. Temperature dependence of the LTEC for americium: experimental data [5] (*1*); lattice component (our calculations) (*2*); and experimental data [6] (*3*); the inset shows the temperature dependence of the bulk compression modulus for americium: experimental data [7] (*1*) and lattice component (our calculations) (*2*).

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